An Investigation of Manometers, of Small Bore, for Use in the Measurement of Osmotic Pressure

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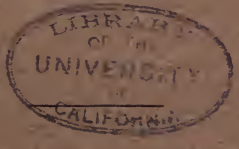
DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH A REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

JOHN LATTIMORE CARPENTER

BALTIMORE
1911



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CONTENTS.

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Dr. Holland and Mr. Cash are due the writers thanks for their willing assistance from time to time.

AN INVESTIGATION OF MANOMETERS OF SMALL BORE FOR USE IN THE MEASUREMENT OF OSMOTIC PRESSURE.

Review of former work.[1]

Throughout the ten or more years of investigation of osmotic pressure in this laboratory a major portion of the time has been spent in the detection and elimination of sources of error. In order that the problem might be attacked upon a secure basis, the following factors must become known and reliable quantities, *viz.:* a suitably strong semipermeable membrane; an effective method for depositing the same; a cell of fine texture, suitable porosity and at the same time possessing great strength of wall; baths accurately and automatically regulated as to temperature; and finally, manometers of a type convenient to manipulate for registration of the pressure exerted within the cell. Examination of the published work will reveal how elaborate and perfect the system has come to be. In fact all the larger difficulties have been disposed of rather satisfactorily except the manometer factor.

Sufficiently accurate manometers for the measurement of the temperature coefficient of osmotic pressure have been in use for three years and their preparation has been described.[2] But it was realized that these instruments had constant error factors—though of uncertain magnitude—and it was with difficulty that an adequate number of the instruments agreeing sufficiently well among themselves were finally obtained. By the methods of manometer preparation formerly used one was by no means certain whether he would obtain a "good" instrument. The worker was constantly

[1] Earlier papers will be found in Am. Ch. Jr., 28, 1; 29, 173; 32, 93; 34, 1; 36, 1 and 39; 37, 324; 425, 558; 38, 175; 39, 667; 40, 1, 194, 266, 325; 41, 1, 92, 257; 45, 91.

[2] Am. Chem. Jour., 40, 325.

fearing the worst and in the majority of cases his fears were realized. However, a series of manometers came into hand which agreed closely, and these were chosen for the measurements.

These manometers have been prepared substantially, as follows: the capillary[1] tubes were chosen with care, extra efforts being made to find those of most uniform bore; the tubes were then calibrated carefully from a scratch on the tube near the bottom of that portion which would be filled with gas. Curves were plotted and the irregularities expressed in "calibration units."[2] Next the capillary depression of the tube was determined as some point, and then the tube was carefully cleaned again, dried and filled in the customary manner with nitrogen. The next step in the procedure was the determination of the volume of gas, expressed in calibration units, contained in the closed manometer. Three methods were used—two differing only slightly from each other. One method was to place the manometer in a steel block and calculate the volume from the known volume of a "standard" manometer. The "steel block" is nothing more than a strong reservoir with receptacles for three manometers and plungers with which to secure a wide range of pressures. From the known volume of the "standard" one could calculate the pressure its gas volume was under. Then with the proper corrections applied to the manometer under comparison one could calculate the volume of gas enclosed at 0°–760 mm. This method soon fell under suspicion for reasons not fully understood at the time—these will be presented later. The other method consisted of the open "side tube" method. The "side tube" consisted of a portion of the same capillary from which the manometer was made. The purpose was to eliminate capillary depression effects. If the side tube was substituted in the steel block in place

[1] The term "capillary" referred to manometer tubing in this paper means a tube varying in diameter from 0.4 mm. to 0.8 mm.

[2] The "calibration unit" is the average volume of each millimeter of the calibrated tube, and is calculated from the weight of a thread of mercury which fills the whole length of the capillary.

of the "standard manometer" the pressure on the manometer under examination was easily obtained. It would be the sum of the height of the mercury column in the side tube, above that in the manometer, plus the barometric pressure. Knowing the pressure and observing the volume of the gas in the manometer and keeping the latter at a strictly constant temperature, it is only necessary to apply the gas law equations to find the volume under standard conditions. A modification of the "side tube" method was to use a tape wound rubber tube as the connecting reservoir between "side tube" and manometer. This economized time, and is equally accurate. After a number of observations had been made at different pressures on the manometer, under examination, the average value of these was assumed to closely approximate its volume. The final test of the manometer however came after it had registered constant pressure when set up in solutions of known pressure capacity, *i. e.*, in terms of the manometers chosen before as probably the most accurate ones. That there was error in the absolute gas volumes of these manometers, and therefore error in the pressures they registered, was recognized. But these errors were small and of such a nature that they exercised negligible effect upon the ratio expressing relation of osmotic pressure to temperature or in other words the temperature coefficient.

A NEW TYPE OF MANOMETER, AND DISCUSSION OF THE SAME.

However, when the determination of absolute osmotic pressure is to be considered—or in other words the relation of concentration to pressure, these errors assume an altogether serious aspect. And while the errors are small, and the labor of eliminating them is tedious and time consuming, still the end hoped for is worthy, or even necessary. The work herein described has been an effort to eliminate as far as possible this last error source—the manometer error factor.

With a manometer of large volume the majority of error sources are no larger than in those of small volume. Hence in those of large volume the percentage error would be greatly reduced. With this idea in mind a new type of

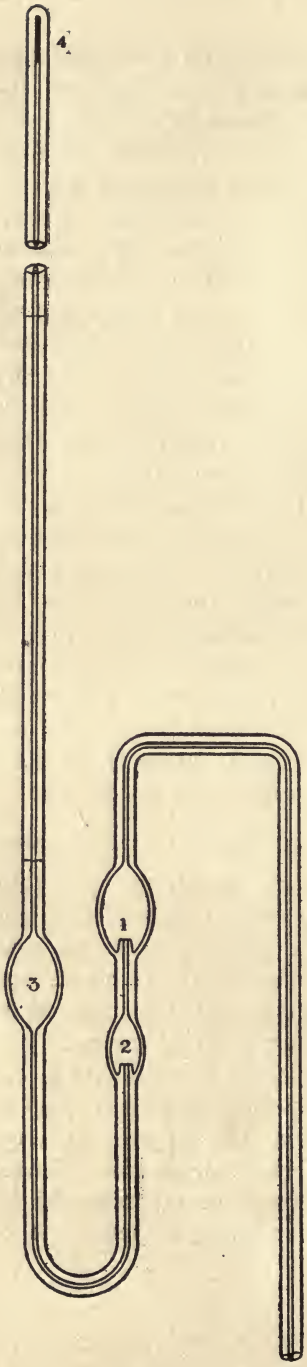


Fig. I.

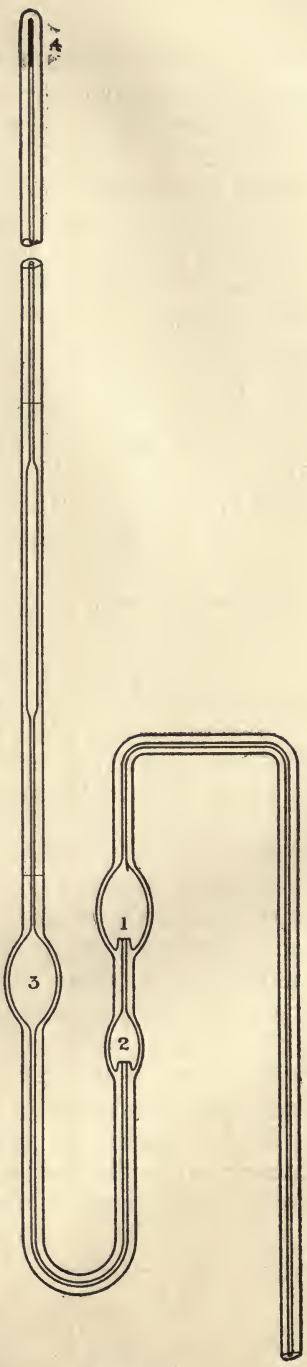


Fig. II.

manometer was devised. Figs. I and II show the old and new type respectively. The type shown in Fig. II has a tube of large bore sealed between the two portions of small bore. The purpose of this is to furnish a large volume without unduly lengthening the instrument. These large tubes are so selected as to length and bore that the instruments may be used only above certain concentrations, that is, a solution must exert sufficient pressure to sustain the mercury at a point several millimeters above the joint of the enlarged portion of the tube and the capillary above. The pressures necessary vary from 3 or 4 to 20 atmospheres for different manometers.

The capillary tubes were selected with the usual care and put into the hands of an expert glass blower. They were returned as straight tubes, extending in length a few centimeters below bulb 3 and not sealed at the top as shown at 4. These tubes were carefully annealed, allowed to rest undisturbed for some months before calibration. These tubes were then carefully calibrated by the usual method in use in this laboratory.[1] From Fig. II it may be observed that small marks cross the capillary a few millimeters above bulb 3 and the enlarged portion of the tube. These marks are known as the "lower scratch" and "upper scratch" respectively, and the small capillaries above them are known as the "short and "long" capillaries respectively. The "long capillary" was first calibrated and the "calibration unit" determined. Next the "short capillary" was calibrated and its curve plotted in terms of the long capillary's calibration unit. Now a thread of mercury was run into the enlarged portion of the tube until it filled the tube from the upper scratch to some point certainly within the calibrated portion of the lower capillary. The length was observed, the temperature likewise and the mercury was run out and weighed. From the data in hand the total volume between scratches was obtained, and this in turn was expressed in the calibration unit of the long capillary. This latter operation was all gone over in duplicate by the writer,

[1] This work was done by Dr. Holland.

and the values obtained agreed very precisely with the former determinations.

DETERMINATION OF CAPILLARY DEPRESSION.

(*a*) *Purification of Mercury.*

The next examination to be carried out was a detailed one for capillary depression. For this purpose and also for filling the manometers, a supply of very pure mercury was necessary. The smallest amount of impurity either dissolved or mechanically held is well known to seriously hamper the free flow of mercury through tubes of small bore. Hence the necessity of very pure material. This had been previously, prepared, and the preparation had best be described here. To obtain pure mercury is no such simple matter as might appear to the inexperienced. Too great care cannot be exercised in its preparation. A high grade mercury was obtained from dealers and was subsequently treated by the writer in the following manner, (1) about four to six pounds were placed in a long-necked, hard glass receiving bulb. This had fitted into the neck a two hole cork stopper carrying two glass tubes, one of which extended below the surface of the mercury and opened into the air without, the other extended just below the stopper and at the other end was attached to a pump. The bulb was placed on a sand bath and heated to the boiling point of mercury for four to six hours, air being drawn through the entire time. The effect was surprising in that a large amount of impurity was oxidized and appeared on the surface as scum. (2) After cooling, and filtering through a paper perforated with pin holes, the now bright metal was introduced into and distilled through a vacuum still. This still was of a simple order, being made from a piece of Carius combustion tubing. The supply reservoir of the still was an ordinary U-tube and from this the supply arm led up to the still proper. This tube was of such a length that by merely raising or lowering the U-tube one could adjust the length of the mercury column to meet barometric changes. The delivery tube was somewhat more than barometric length and hence always maintained a column

of mercury sufficient to offset atmospheric pressure. The upper portion of the delivery tube was somewhat enlarged so that the mercury would have greater condensing surface, and so that, in falling, air was continually being trapped and carried out. Once the still was in operation it gradually kept refining its own vacuum. (3) The mercury was next washed by the method of Lothar Meyer. Instead of ferric chloride solution, however, a two per cent. nitric acid and two per cent. mercurous nitrate solution was used. A very effective means of breaking the mercury into fine globules was employed by the use of a silk bolting cloth strainer. A half liter separatory funnel was flared somewhat at the delivery stem and over this was bound a double thickness of the cloth. On opening the stopcock and allowing the mercury to enter it breaks into perhaps many thousands of fine globules. In fact the separation is so effective that the whole length of the two meter verticle tube, through which it falls, is darkly and heavily clouded. This exposes an enormously large surface to the action of the acid and salt. Futhermore the pouring was repeated 1000 times. By continually renewing the solution it would seem quite safe to think that all those metals which are volatile with mercury vapor, and hence had not been left behind in process (2) would be removed. (4) After washing with water, drying and filtering again, the mercury was finally redistilled through a second vacuum still. This still was of the same type as the one described above, but very much smaller. Before use in a manometer this mercury was filtered again, either through hard filter paper perforated with pin holes, or through a clean funnel drawn to a capillary at the end. The latter has the advantage that it offers no lint or dust to stick to the surface of the metal. An entirely satisfactory grade of mercury was thus obtained.

(*b*) *Discussion of Capillary Depression.*

The fact that it has been found most practicable to determine manometer volumes at low pressures caused the capillary depression factor to assume altogether important

proportions. As mentioned above it was sought to escape this factor, in so far as it affected volume determinations, by the use of the "side tube" cut from the same piece of tubing as was the manometer. That it did not eliminate the error, but probably introduced one will be shown later.

The procedure of determining the capillary depressions was very simple. A tube 40 mm. in diameter and 25 cm. long was used as the reservoir. This was sealed to a short piece of ordinary thick-walled barometer tubing, and manometer and reservoir were connected by a suitable length of tape-wound rubber tubing filled with mercury. Before attaching the rubber tube to the manometer the latter was supplied with a sufficient quantity of the pure mercury to render it certain that the meniscus would be clean and the flow of the mercury free. The point at which the meniscus stood could be varied at will by raising or lowering the reservoir.

This work was carried out in the "Manometer house," which is kept at a constant temperature—and will be described later. Hence the probability of error from fluctuating temperature was avoided.

Since the effect of capillary depression was most serious as to its bearing upon volume determinations, and since the meniscus in the manometer would stand somewhere in the short capillary while its volume was being determined, it is at once apparent that a detailed examination of that portion of the manometer should be carried out. The capillary depressions were ascertained at shorter intervals and with more precaution as to tapping in the short capillary than in the long capillary. Of course as the pressure increases in a manometer the capillary depression error decreases, and indeed above a few atmospheres become quite insignificant.

The tendency on the part of the mercury to lag in the small capillary was overcome by tappers. These were the ordinary coils and hammer of small call bells, mounted upon weighted standards. These could be easily placed in a suitable position and controlled by a button on the outside of the manometer house. If it were left to these tappers alone

to establish equilibrium between the columns it frequently required more than an hour. However, the operator found that a preliminary tap or two on the connecting rubber tube with a pencil would so hasten equilibrium that only ten to fifteen minutes subsequent tapping by the hammers was required.

It has been suggested that it is unnecessary to go through the labor of experimentally determining the capillary depression of small bore tubes. That instead of such experimental determination the depressions could be calculated directly from the surface tension value of mercury and the diameter of the tube, expressed by the following equation.

$dgh = \frac{2T}{r}$ or $h = \frac{2T}{dgr}$, where h would represent the depression, T the surface tension of mercury in dynes per centimeter, d the density of the mercury at the temperature observed, g the gravitational constant, and r the radius of the tube. Such a calculation would be entirely satisfactory if one could be certain of the values of T and r. The value of T, however, is so strictly a function of the purity and cleanliness of the mercury that it is not without risk that the commonly accepted values are adopted. Futhermore, no scruple must be spared in cleansing the capillary tubes. These two factors—the mercury and the tube—place the investigator in a dubious frame of mind as to how well some one else's value for T will fit his own needs. Equally as serious, or probably more serious, is the unreliability of the value for r at any particular point. To determine the diameter of a capillary tube exactly, at points very slightly removed from each other, through any considerable length of a tube would involve an enormous amount of time and labor. Slight irregularities only a millimeter or two apart cause very marked differences in capillary depression, hence it is not without grave risk that the mean diameter through even a short distance may be adopted. Nor is it in any measure safe to determine the capillary depression at one or two points and adopt the mean as the true depression for all points.

The accompanying Table I will furnish some idea of how variable depressions may be at points not remote from each other, even though the tube has been chosen with utmost care. The manometer was of the old type, as shown in Fig. I, and is, for certain laboratory convenience, designated M. 5.

TABLE I.

Distance above scratch.	Capillary depression.	Distance above scratch.	Capillary depression.
8.65	7.92	117.43	11.42
22.70	10.85	224.12	11.18
47.35	9.87	280.30	11.74
71.38	10.04	361.10	11.80
114.28	10.42	414.10	12.14

Now since pressures ranging from 800 to 1000 millimeters constitute the limits between which one must determine the volumes of these manometers if open side is used, any considerable discrepancy in capillary depression would have a grave effect on the accuracy of the final result. In fact, at such low pressures, a difference of one millimeter amounts to a difference of about one calibration unit when the final volume is calculated. If in the case of manometer M. 5 the depression had not been taken nearer the scratch than 22.7 millimeters, and the observations carried out from that point as tabulated, by former usage the mean value 11.05 of these last nine observations would have been adopted. If now the manometer had been filled with nitrogen, and sealed and its volume under process of determination, unless sufficient pressure were brought to bear to bring the meniscus above 22.7 mm. from the scratch an uncertainty at least would be introduced as to the final gas volume in the manometer. If the meniscus could not be brought above 9 millimeters above the scratch, and if the mean depression value of 11.05 were assumed to be the depression at that point, an error of $11.05 - 7.92 = 3.13$ calibration units would have resulted. The volume of this manometer, subsequently determined, was 503.00 calibration units. An error of 3.13 calibration units would have caused an error of about 0.62 per cent. on the volume. While this error would have de-

creased as pressure increased still it would have furnished sufficient discrepancy from other instruments to stimulate distrust in its accuracy. Hence, as has been stated above, very detailed determinations of capillary depressons were made in the short capillaries of the manometers, and careful though less detailed determinations in the long capillary. Curves were plotted for depressions in the same fashion as for calibration.

FILLING THE MANOMETERS.

(*a*) *The Preparation of the Nitrogen.*

The manometer tubes were now considered ready for filling with nitrogen. To the stem below bulb 3, Figs. I and II, the straight tube carrying bulbs 1 and 2 was sealed and subsequently bent as shown in the figure. To be quite satisfied as to the cleanliness of these tubes—now unfilled manometers—they were subjected to a third cleansing with sulphuric acid chromic acid mixture, washed out with distilled water, and finally washed several times with "conductivity water." They were then placed in a drying train, and dry air pumped through for not less than 18 hours.

Mention has been made, in a paper[1] already published, of the fact that air was at one time used to fill the manometers and that nitrogen was subsequently adopted. When air, however, carefully washed and dried, was used, there seemed ultimately to be a decrease in the volume of the gas in the manometer. This could be due to oxidation of impurity in the mercury—as oxidizable impurity might have been present. The adoption of nitrogen has eliminated that trouble. The preparation of the nitrogen was marked by the same care which was exercised in all the different steps of the work. The nitrogen was prepared from air in the following way: The air was drawn through a train of bottles containing alkali pyrogallate, continuing through a tube at red heat containing reduced copper, then on through wash bottles containing alkali pyrogallate and concentrated sulphuric acid respectively, thence through another tube

[1] *Loc. cit.*

at red heat containing first copper oxide wire then reduced copper gauze, thence through tubes of fused calcium chloride and stick caustic alkali, and finally through a tube of resublimed phosphorous pentoxide distributed over asbestos fiber. The whole train was filled, heated, and air drawn in for some time. Then it was closed and allowed to stand for some hours in order to give opportunity for a diffusion from all packed places of any oxygen or other gas that could be separated out. After reheating, and drawing in a current of air for some time and allowing the nitrogen to waste, the reservoir was finally attached and a supply of nitrogen collected.

(*b*) *Filling and Closing the Manometer.*

The method of filling the manometers was the same as that used in former work, *viz.:* the mercury was first drawn into bulbs 1, 2 and 3. Then the manometer is sealed at the top to a stem from the nitrogen reservoir. The nitrogen is used to wash the manometer free from air several times before it is finally closed. After allowing the desired quantity of gas to enter, the usual mercury thread is run in at the top, and the manometer sealed off as described in a paper already referred to. Only one modification of the process was adopted. Formerly, when the top of the manometer was being sealed off, the short mercury thread immediately underneath the play of the blow pipe flame often became so agitated—due to sudden vaporization and condensation of its top portions—that globules frequently became detached and trapped gas between themselves and the main thread. This caused much trouble, and frequently required reopening the manometer for their dislodgment. This was remedied by simply softening the walls of the tube, somewhat above that portion at which the upper meniscus would stand, and allowing the capillary to become constricted to very fine bore. This measure hindered the rapid vibration back and forth of the column and not a single accident was experienced in the entire lot of manometers.

DETERMINATION OF GAS VOLUMES.

Since the object of this entire investigation was the develop-

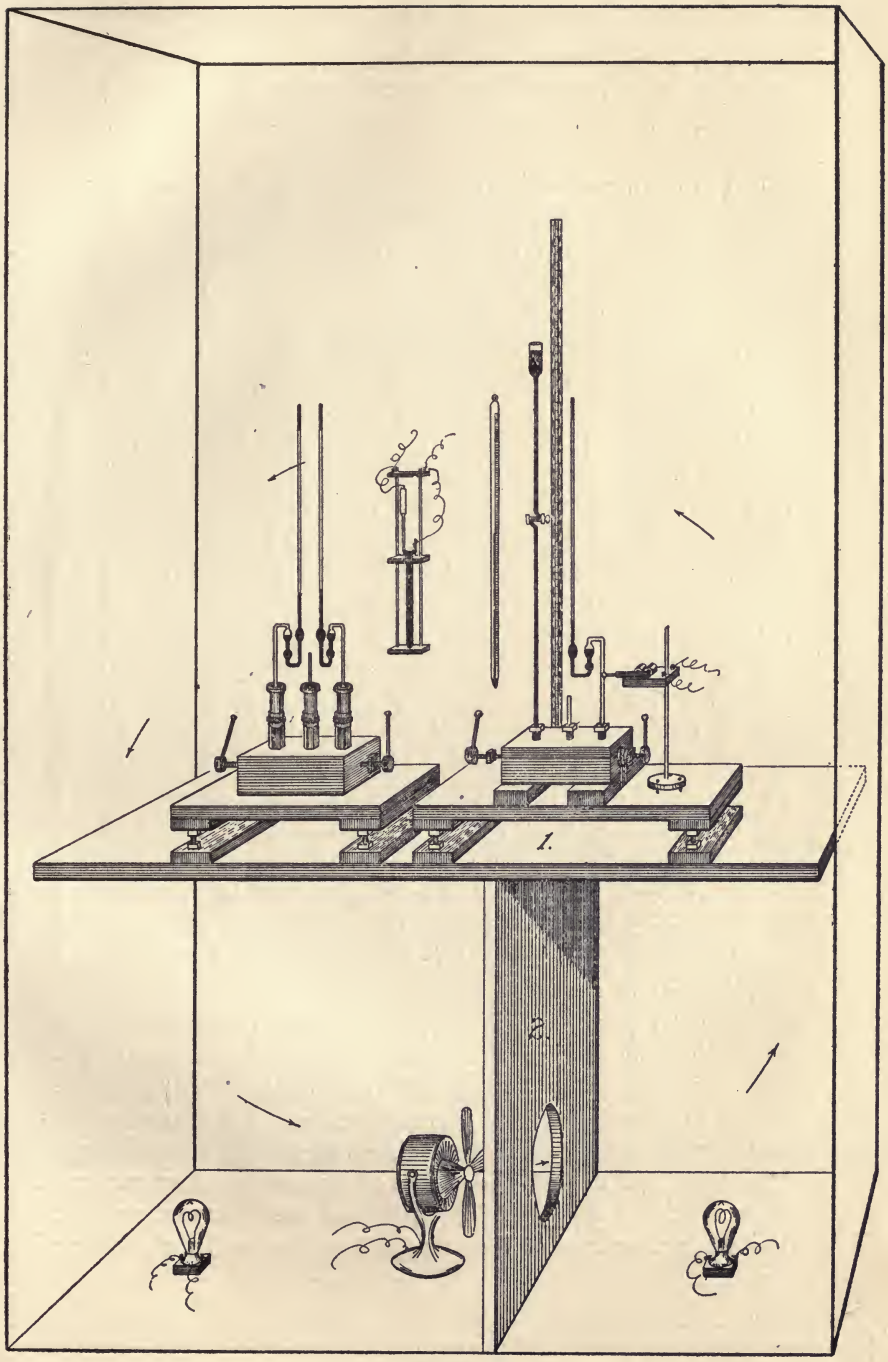


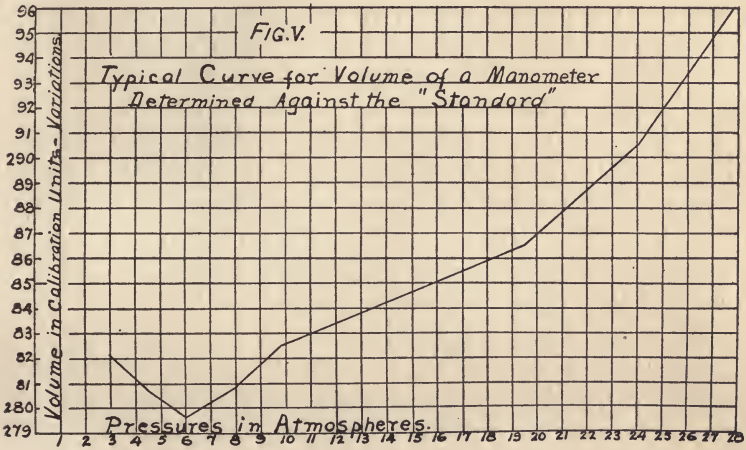
Fig. III.

ment of a reliable method for manometer construction, and since up to this stage of the work no pains or time had been spared for the sake of accuracy, it was necessary here to hit upon the most reliable method of work also. Much care was taken to arrange a bath which would conveniently accommodate all the necessary apparatus, and at the same time be easily regulated at a constant temperature. This bath is known as the "manometer house." All the essential details are shown in Fig. III. In the figure (1) is a shelf on which is arranged all the instruments, such as the "steel block" the "brass block," the meter scale, the tappers, etc. This shelf rests on heavy brackets which are bolted to the heavy masonry of the wall behind. The thermoregulator is hung from a bracket on the wall itself and is thus freed from the effects of the vibrations caused by the tappers when these are at work. Partition (2) merely serves to hold back the air and necessitates its being forced by the fan motor through the hole in the partition. The arrows show its direction of circulation. At each end of shelf (1) a 5 cm. space allows the air to pass through the upper compartment. This bath is kept a few degrees above the temperature of the outside room—this latter being regulated roughly by a steam radiator or a gas stove. Control of temperature is maintained by the lamps shown in the figure—the lamps being controlled by the thermoregulator above. In fact the system of the electric control of heat is identical with that in use in all the constant temperature baths employed in this work. With this arrangement, fluctuation of temperature is kept well within 0.1 of a degree. More minute details of the manometer house are shown from Fig. IV.

The steel block, which has been previously described, was orginally designed for the determination of manometer gas volumes against a "standard" manometer. The volume of the proposed standard was determined at low pressures—but without the precautions observed in the recent work. The idea was to find the means of comparing other manometers under high pressure with this one. Assuming that the original volume of the standard was correct, the pressure

Fig. IV.

it would be under at any position of the meniscus could be easily calculated from the gas laws. Further, if another manometer was in series with it, if proper corrections were applied for the different heights of mercury, the pressures must have been identical. From this pressure the volume of the second manometer was in turn calculated. No satisfactory results were ever obtained by the "standard" manometer method. At low pressures a different volume was always calculated than at high pressures. In Fig. V is shown



a typical curve for the "volume" of nitrogen in a manometer determined by this method. Obviously, a volume curve of a closed manometer is a straight line. Hence some constant error was affecting the results. It is more probable that two factors were at work. That one which was most effective under low pressure was probably due to capillary depression. That under high pressure appears to have been due to error in meniscus correction. The former error would decrease in importance as the pressure was increased, while the latter error would increase in marked proportion with increased pressure.

The proper meniscus correction has been a much mooted question, and confession must be made that no method

without theoretical or practical objection is at hand. It is stated that perfectly pure mercury leaves perfectly pure glass at an angle of 148 degrees. The determination of such an angle would not be difficult from a plane surface, or from a cylindrical surface provided the arc of curviture of the latter was sufficiently great to furnish a tube of such diameter that capillary effects were overcome; but in a tube of very small bore such determination would be a difficult matter. To assume that the meniscus in tubes of small bore is hemispherical, approaches the true state of affairs but falls somewhat short of the mark. However, we have found the correction based on such an assumption to be perhaps the best available, and such correction has been applied in this work. The method follows: "Assuming that the surface of a meniscus is similar in shape to half a sphere and that the two surfaces of a double meniscus are equivalent to an entire spherical surface the following conclusions may be drawn: In a manometer there are a number of cylinders, each capable of containing a definite number of cubical units, the number of which would depend upon the position of the menisci at the time a volume was included.

"Since the volume of a cylinder $= \pi R^2 h$, where R = radius of the circular section, and h = the height; and since the volume of a sphere $= {}^4/_3 \pi R^3$, and considering the sphere incribed in the cylinder, then the volume of the double meniscus is equivalent to the difference in volume of the cylinder and the inscribed sphere. $\pi R^2 h - {}^4/_3 \pi R^3 = x$; $h = 2R$. Then $\pi R^2 h = 2 \pi R^3$; $2 \pi R^3 - {}^4/_3 \pi R^3 = {}^2/_3 \pi R^3$ = volume of double meniscus.

"Now since this expression above is in cubical units and the volume of the manometers is expressed in linear units, the former must be converted also into linear units.

"Now ${}^2/_3 \pi R^3$ = volume in cubical units

πR^2 = area in cross section

${}^2/_3 \pi R^3$ divided by $\pi R^2 = {}^2/_3 R$ = volume in linear units. ${}^2/_3 R = {}^1/_3 D$. Hence, by determining the mean diameter, the meniscus correction is at once obtained."

By a recent recalculation of a series of volume determinations on a manometer which was compared with the "stand-

ard," upon application of the revised meniscus correction, the curve shown in Fig. V was straightened out somewhat at higher pressures. This seemed to fix the trouble upon that factor. The importance of the meniscus correction may be seen from the following extract from a paper[1] on this work:".....in determining the temperature coefficient, the errors in the meniscus correction, if they are uniform, may be very large without seriously affecting the result; but when it is attempted to ascertain the relation of osmotic pressure to concentration, the case is very different, for then the pressures of all the various concentrations of solution are to be compared at fixed temperatures, and the meniscus corrections have consequently widely differing values. This is illustrated from the data taken from the record of a single manometer (No. 9). The meniscus correction (double) in this instrument is 0.17 calibrations unit, and the volume of nitrogen under standard conditions of temperature and pressure is 454.14 calibration units. Column I in the table gives the weight normal concentration of the solutions; II, the pressures in atmospheres; III, the volume of the compressed nitrogen reduced to standard temperature; IV, the corrections in fractions of an atmosphere for the double meniscus; V, the relative osmotic pressures, the pressures of the 0.1 normal solution serving as the unit. Column VI contains the relative corrections for meniscus, the correction for the 0.1 normal solution serving as the unit. The temperature in all cases is 25 degrees.

I. Conc.	II. Os. pres. atmos.	III. Vol. nitrogen cal units.	IV. Men. cor. atmos.	V. Rel. os. pres.	VI. Rel. men. cor.
0.1	2.635	141.15	0.00317	1.0000	1.0000
0.2	5.139	80.69	0.01083	1.9503	3.4164
0.3	7.738	55.59	0.02566	2.9366	7.4637
0.4	10.295	42.41	0.02126	3.9070	13.0158
0.5	12.947	34.01	0.06972	4.9135	21.9937
0.6	15.620	28.37	0.09360	5.9275	29.5268
0.7	18.436	24.11	0.12999	6.9928	41.0063
0.8	21.258	20.97	0.17233	8.1055	54.3628
0.9	24.126	18.53	0.22133	9.1558	69.8202
1.0	27.076	16.54	0.27834	10.2755	87.8044

[1] Am. Chem. Jour., 45, 237.

Particular attention is called to columns V and VI, where it will be seen that, while osmotic pressure increased a little over ten fold, the value of the meniscus correction increased nearly 88 fold."

As was stated earlier in this discussion of the standard, no means was ound of avoiding discrepancies in volumes of compared manometers under low pressures. It is reasonably certain however that these are due to variations of capillary depressions. And since no way of ascertaining these was at hand without opening the manometer and experimentally determining the depressions the "standard" was discarded.

The next method used was that of "side tube." This side tube consisted of a piece of tubing cut from the same piece of tubing as the manometer itself, the object being, as has been stated, to avoid capillary depression corrections. In some instances concordant volumes were obtained from several observations. The range of pressures was necessarily limited, as has been explained before. But even through this narrow range of pressures, too wide variations were frequently found to be ascribed to errors of observation. It was found that the errors of capillary depression in the manometer tube and the side tube of presumably the same bore were in a great majority of cases, if not in fact always additive. In such a case as that recited in Table I, errors arising in this way would render the manometer quite worthless, and the time spent in its preparation, as well as that in its use, would be lost.

In order to avoid such liability to error in determining the volume of nitrogen under standard conditions, a side tube 40 mm. in diameter was adopted—the same tube, in fact, that was used in capillary depression determinations. One of these tubes was sealed on to a barometer tube of ordinary bore and about 60 cm. length. The tube carried a stopcock so that the column of mercury might be maintained while changing manometers in the block. This tube is represented in Fig. III. Results obtained by use of this tube were highly satisfactory. Two objections arose to its use however.

It was impossible to vary the pressure even a few millimeters; and furthermore the constant insertion and removal of manometers to and from the 'steel blocks" augmented the chance of accident and breakage, further the process was very slow. The method which proved most satisfactory of all, and that which was adopted, was the use of the wide side tube, by rubber tube connection with the manometer. In fact the same fashion after which capillary depression was determined—the difference being that now the manometer was closed where before it was open. Comparisons were made on manometers by the side tube method, using the capillary tube of presumably the same bore as the manometer, both in the steel block and by rubber tube connection, against the values obtained when the wide side tube was used both in the steel block and by rubber tube method. In the case of the narrow side tube no satisfactory agreements in volume from several observations at different pressures could usually be obtained. With the wide side tubes the agreement was quite satisfactory both in the block and rubber tube, and furthermore these values agree closely with each other. Having established the reliability and expediency of the method, work was immediately carried through on the entire lot of the new type manometer. The procedure was briefly as follows. Manometer and side tube were connected by means of the rubber tube. (In order to avoid refilling the side tube and rubber tube at each change of manometers, a screw clamp was used to close the rubber near the manometer stem before removing the latter.) In this operation care was taken to admit no air into the stem of the manometer. Both side tube and manometer were clamped firmly into position, and small mirrors bound on at a suitable angle for reflection of light to the telescope. A tapper was placed in position against the manometer; and the whole system was then allowed to come to constant temperature of the bath. After temperature equilibrium had certainly been established, and after effective tapping of the manometer, the following observations were taken: Volume of gas in manometer between the two menisci, barometric pressure and temperature, height of

mercury column in the side tube above the lower meniscus in the manometer, and the constant temperature of the manometer house. After making the proper corrections and applying the gas laws, the volume of gas contained in the manometer under standard conditions of temperature and pressure was obtained. The pressure on the manometer could be varied in a limited degree by raising or lowering the side tube. This fact was of prime importance, for it made it quite possible to bring the lower meniscus to a portion of the capillary in which its depression was accurately known. On such days when much fluctuation of the barometer took place, it was difficult to control the exact position of the meniscus, for as atmospheric pressure increased the mercury column in the manometer would rise, and contrary, when the pressure of the atmosphere decreased, the mercury column in the manometer would fall. In such cases the curves plotted for the depressions usually furnished the necessary data for the corrections. However, in a few instances these failed. The latter fact was probably due to some variation of depression which had still escaped the very detailed examination for the same. In such cases the side tube was raised or lowered until the meniscus in the manometer stood in a portion of the capillary where the depression was more constant.

With the exception of two of the manometers of the new type, all gave volumes, under standard conditions, of more than 1000 calibration units. And the largest volume of all was somewhat more than 3200 units. In the case of the old type of manometer it was possible to obtain at most only about 800 units, and in most cases the volumes ranged from three to five hundred units. Since the calibration unit is a linear unit, and not a cubical unit, it is obvious that the size of the capillary controlling the calibration unit would have no influence on the number of units, in so far as increasing or decreasing that number is concerned, if the bore was of the ordinary uniformity. Hence it was impossible to increase the number of units greatly except by lengthening the tube. This was impracticable, and was rendered unnecessary by the adoption of the new type of instrument.

In determining the volumes of manometers, it is impossible to get values agreeing any more closely, in fractions of calibration units, with the old type of manometer than with the new type. Hence, if the actual fractional agreement is as close in a manometer of large volume as in that of one of small volume, the percentage error in the one of large volume is much smaller than that in one of small volume. In most of these manometers, extreme variation of the maximum or minimum volume, determined by observation, from the mean of all the values varied from 0.03 to 0.1 per cent. The variations fall well within the limits of errors of observation.

COMPARISON OF MANOMETERS.

One more step was taken before the manometers were considered ready for osmotic pressure work. And this step would prove the worth or unfitness of the instruments. They were compared against each other. That is to say, two manometers were connected in such a way that their gas volumes were under the identical compression. The comparisons to the present have been made at low pressures only.

In order to compare two manometers against each other, at low pressures, they were connected by the same rubber tube used in the methods for determination of capillary depressions and volumes. Instead of side tube and manometer, there was now placed manometer and manometer. The same precautions were used, as before, to see that the rubber tube and stems of manometers were entirely filled with mercury and free of air bubbles. By adjustment of one of the manometers, up or down, the meniscus of each could usually be brought to a desired point on the short capillary. Tappers were set is position against the instruments and the system allowed to come to the constant temperature of the manometer house. The procedure of observations was identical with that in the determination of volume, except no barometer readings were necessary.

Obviously, when corrections for difference in height of the mercury columns in the two manometers, and capillary depressions, are applied, the pressures on both volumes of

gas must be identical. And if the values for the volumes, obtained by the method set forth in this paper, are correct, then the calculated pressures from these volumes should be identical.

Those three manometers which showed, at once, smallest variation in calibration corrections, capillary depression, and percentage variation from mean in volume, were chosen as standards of comparison. These three are known respectively as numbers 31, 40 and 41.

In Table II is shown a series of results obtained. The columns respectively represent the following: (1) the number of the manometer; (2) the value of the gas volume in the manometer under standard conditions, the value being obtained by the method described in this paper; (3) the observed volume of the slightly compressed gas; (4) the corrected pressure in millimeters calculated upon the assumption that the value in column 2 was correct; (5) corrected pressure expressed in atmospheres; (6) the volume at standard conditions, calculated from pressure of the other manometer as a standard; (7) percentage expression of variation from original value of volume; (8) percentage error distributed between the two manometers.

It will be noticed in the following table that manometer 32 was compared against each of the three chosen standards. It agrees quite exactly with numbers 40 and 41, and agrees very closely with number 31. Furthermore numbers 31 and 40 were compared against each other and agree very satisfactorily. Such a method of procedure makes it possible to place all the instruments on the same basis.

Seventeen of the new type manometers were carried through the operations described in this paper. Out of the seventeen, two (Nos. 25 and 30) are looked upon with suspicion. In Table II is given the reason for suspecting some error in number 30. The volume, as calculated for column 6, is far too small to be accounted for through experimental error, and since number 41 is in such close accord with the other manometers, it is but the natural and necessary course to regard the value in column 2 for manometer 30 as wrong.

TABLE II.

1.	2.	3.	4.	5.	6.	7.	8.
31	1204.53	1038.67	894.03	1.176	1200.62	0.32	0.16
34	954.66	895.10	890.88	1.172	958.06	0.35	0.17
40	1103.75	947.10	938.31	1.234	1103.75	0.00	0.00
32	1212.88	1079.77	938.27	1.234	1212.88	0.00	0.00
41	1676.64	1682.46	832.40	1.096	1677.40	0.05	0.03
36	1302.19	1154.77	832.78	1.096	1301.68	0.04	0.02
31	1204.53	1063.73	945.86	1.244	1201.14	0.23	0.14
40	1103.75	959.98	946.21	1.241	1106.70	0.27	0.13
32	1212.88	1112.52	808.73	1.091	1212.05	0.07	0.04
41	1676.64	1689.69	809.96	1.090	1677.90	0.06	0.03
31	1204.53	1072.29	894.56	1.177	1201.91	0.22	0.11
32	1212.88	1135.57	892.16	1.174	1216.14	0.26	0.13
41	1676.64	1697.55	825.01	1.086	1701.81	1.50	0.75
30	1407.55	1294.37	837.40	1.101	1388.49	1.35	0.67

Number 25 presents a similar discrepancy, although of small magnitude. However, the errors are too large to warrant the use of the manometer, in both cases, in osmotic pressure work, until their nitrogen volumes, at standard conditions, have again been carefully determined.

Any percentage error in volume, as expressed in column 7 of Table II, is the whole error of the two manometers. Now, since the two manometers are connected by free-flowing mercury, the case is not unlike that of a balance. If one arm of the balance moves in one direction, the other arm moves in the contrary direction. Then, in the case of the two connected manometers, even a small displacement of equilibrium, for any cause whatsoever, would divide itself between the two instruments. Therefore it is unfair to make one monometer carry the error of the two. For this reason the writer believes that column 8 expresses the real error more closely than column 7.

The comparisons of these manometers will be carried on under pressures as high as 28 to 30 atmospheres. For this work the "steel block" and the "brass block" will be used. The brass block differs from the steel block in that its reservoir contains water, and that manometers may be placed into it in the same fashion as they are placed in the cells for an osmotic pressure measurement.

SUMMARY.

1. The earlier work on manometers has been reviewed, and its inaccuracies taken into account.

2. A new type of manometer has been devised. Its advantages over the older type have been pointed out and discussed.

3. The method of calibration of these manometers has been reviewed.

4. A supply of very high grade mercury has been prepared and the method described.

5. The method of determining capillary depressions of the manometer tubes has been dealt with and the purpose fully discussed.

6. A review of the method for filling the manometers with nitrogen, and of closing the instruments has been given, and the method of preparation of the nitrogen gas has been described.

7. The apparatus, bath, and method of calculation for determination of gas volumes, at standard conditions, of the manometers has been described.

8. Comparisons of all the new manometers have been made against each other at low pressures; and 15 satisfactory instruments have been obtained.

9. The object of the work was to throw light on error sources of manometers of small bore. Although much remains yet to be done, it is believed that some progress toward the end has been made.

BIOGRAPHY.

The writer was born on a farm, six miles west of Brooksville, Mississippi, on May 10th, 1884. He was awarded the B.S. degree, from Mississippi College, Clinton, Miss., in June 1904; A.M., *Ibid.*, 1905. He has spent three years in residence in the Johns Hopkins University.